Evidence of a Temperature-dependent 'Blueschist' to 'Eclogite' Transformation in High-pressure Metamorphism of Metabasic Rocks

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ABSTRACT

Textures in the blueschist metabasic rocks of the island of Syros, Greece, indicate a reaction forming omphacite and garnet from earlier glaucophane and epidote. A balanced 'whole rock' reaction can be written using the phase compositions and modal mineralogy of the products observed. This reaction is continuous in P–T space if Mg and Fe^{2+} are independent components. The available thermodynamic data suggest that the 'eclogite' (garnet plus omphacite) assemblage is favoured by higher temperatures.

It cannot, however, be conclusively shown that the rocks went through an up-temperature interval of metamorphism. The reaction seen could be promoted by reduced silica, or water activity. The details of the reaction textures and mineral zonation patterns show furthermore that chemical equilibrium was not maintained throughout the rock development. The reaction textures differ in detail in different samples. In those samples in which the textures are most consistent with maintained chemical equilibrium however, the mineral zonation patterns do imply up-temperature metamorphism.

INTRODUCTION

The purpose of this paper is two-fold—firstly, to report evidence from a suite of high-grade blueschist facies rocks that suggests a reaction relationship between glaucophane-bearing assemblages and eclogites, and secondly, to illustrate the general absence of complete chemical equilibrium in the histories of these rocks.

The relationship between glaucophane-bearing metabasic rocks and eclogites in high pressure metamorphism has been a matter for debate amongst petrologists. The formation of one rather than the other assemblage has been variously ascribed to: differing pressure and temperature conditions (Reinsch, 1979), differing bulk compositions at invariant P–T conditions (Dixon, 1969; Brown & Bradshaw, 1979; Schliestedt, 1980), and the presence or absence of a fluid phase, or the water content of the fluid phase (Fry & Fyfe, 1969; Lappin, 1974).

In metabasic rocks from the Aegean island of Syros reaction textures showing the growth of garnet and omphacite over a glaucophane–epidote assemblage are preserved within single samples of thin-section size. The field relations of these rocks suggest that the reaction seen could potentially have resulted from a change in any of the metamorphic variables listed above. A further possibility here is that the reaction seen is the result of the progressive equilibration of a non-equilibrium assemblage (Dixon, 1969). In view of the debate over the relationship between glaucophane-bearing metabasites and eclogites, and in view of the possible use of metamorphic P–T paths in constraining tectonic models it is useful to be able to determine which of the various possibilities gave rise to the reaction as seen here.

The approach to this problem explored here uses the zonation patterns of the phases present to determine the change in the equilibrium of each of a series of reactions that can be

written between the components of these phases (Holland & Richardson, 1979). There will be some reactions which distinguish, for instance, between a change in cation activity and temperature.

The first half of this paper describes the reaction textures seen, and examines the form and nature of the inferred chemical reaction. The second half discusses those features of the textures and the mineral zonation patterns that show that equilibrium was not in general maintained, and suggests which features may most reliably reflect equilibrium development.

REGIONAL GEOLOGY

High-pressure, but often partially overprinted assemblages ranging from gl–law to omph–gar–gl facies (for mineral abbreviations used throughout the text see Table 1) are seen over much of the Cycladic area of the Aegean (Fig. 1). This area of metamorphic rocks has been termed the Attico-Cycladic crystalline massif. The high-pressure metamorphism over the whole area has been dated as Eocene (Andriessen *et al.*, 1979, K–Ar and Rb–Sr techniques; Blake *et al.*, 1981, $^{40}Ar/^{39}Ar$ determinations). For a recent description of lithologies and assemblages present see Dürr *et al.* (1978).

Syros forms part of the belt within this crystalline massif that shows the highest grade (gl–omph–gar) blueschist facies metamorphism. The rock sequences on Syros are predominantly metasedimentary—alternating marbles and pelitic units with some intercalated metabasites (Dixon, 1969; Ridley, 1982). The rocks are intensely deformed with an almost completely penetrative layer-parallel and flat-lying metamorphic foliation. The sequence is at least in part tectonically constructed. There are isolated serpentinite lenses at discrete levels within it (Van der Maar, 1981), and suggestions of large scale isoclinal recumbent folds (Papanikolaou, 1980).

The metamorphic conditions for the northern half of Syros are well defined (Fig. 2). The assemblages jadeite + quartz, zoisite + paragonite + quartz, and lawsonite, but not lawsonite + jadeite indicate temperatures of 450–500 °C at a minimum pressure of 14 kb (Dixon, 1976; using the data of Crawford & Fyfe, 1965; Newton & Smith, 1967 and Chatterjee, 1972). The blueschist assemblages are generally well preserved. There is a local partial overprint by lower-pressure, greenschist-facies assemblages.

A suite of variegated meta-igneous rocks, predominantly metabasites, but with small volumes of leucocratic, acidic rocks, and some serpentinite slices outcrops along a 3 by 1 km belt in the north of Syros (Dixon, 1969; Ridley, 1982) close to the top of the sequence on the

TABLE 1

Mineral-name abbreviations

act	actinolite–tremolite
chl	chlorite
di	diopside
ep	epidote–clinozoisite
gar	garnet
gl	glaucophane
gro	grossular
jd	jadeite
omph	omphacite
par	paragonite
pyr	pyrope or pyrope + almandine
qtz	quartz
rut	rutile
sph	sphene
law	lawsonite

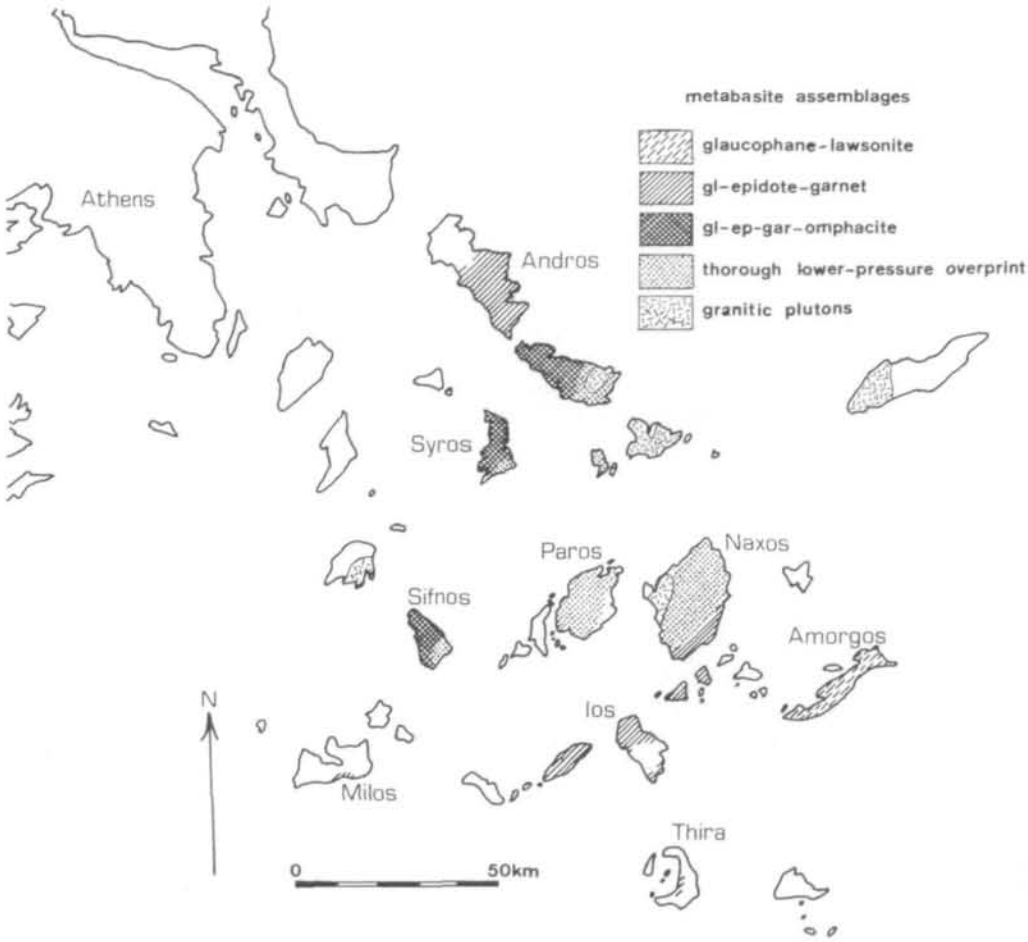

FIG. 1. Location map for Syros and the high-pressure metamorphic rocks of the Cyclades showing the division of the crystalline rocks by blueschist metamorphic grade.

island. The metabasites are texturally very varied with locally differing intensities of deformation. This paper will concentrate on the textures and petrology of the pervasively foliated, gneissic metabasites. The undeformed and partially deformed rocks display petrological complications arising from a change, on the onset of deformation, from local to bulk equilibrium. These complications are discussed separately elsewhere (Ridley & Dixon, 1984).

PETROGRAPHY

The assemblage within the metabasites in approximate order of mineral abundance is:

$$gl + ep + gar \pm omph + mica \pm qtz + rut \pm sph \pm chl + opaques.$$

Both paragonite and phengite have been detected in all samples analysed but are indistinguishable optically. Opaques are ilmenite and/or haematite. Almost all samples show textures indicating the relatively late growth of omphacite and garnet over glaucophane and epidote (for descriptions see following section).

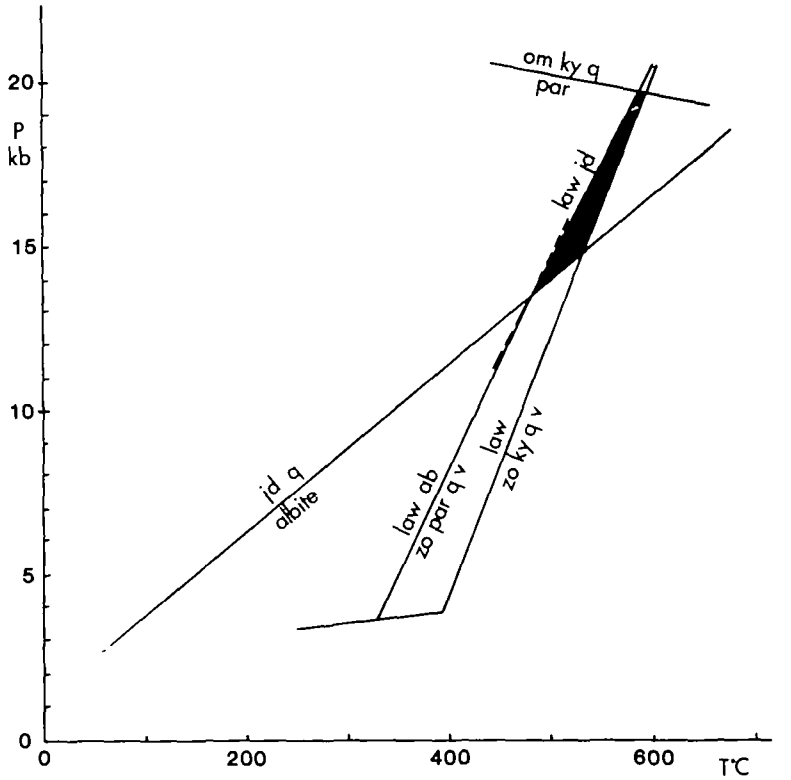

FIG. 2. Critical reactions defining the conditions of high pressure metamorphism in the north of Syros, after Dixon (1976) with the addition of the upper pressure limit of paragonite stability after Holland (1979). (Abbreviations: ab–albite, jd—jadeite, ky—kyanite, law—lawsonite, om—omphacite, par—paragonite, q—quartz, z—zoisite.)

Metabasites immediately adjacent to the serpentinite bodies, and those as included blocks within them show metasomatically influenced high-variance assemblages, often with monomineralic rims at the contact itself. These are not considered further.

Textural evidence for an 'eclogite' producing reaction.

The schistosity in the gneissic metabasites is defined by a polygonal, well annealed glaucophane fabric forming 30–70 per cent of the rock. Grain size is generally very constant at around 100 μm. The glaucophane shows a strong crystallographic fabric but is generally only weakly elongate.

Epidote forms 20–40 per cent of the rock. It is seen as scattered weakly elongate grains, or more rarely concentrated in discrete layers. Its grain size is similar to that of glaucophane.

The glaucophane fabric shows many of the features expected of a steady-state, dynamically recrystallized fabric (White, 1977; Means, 1981). It remains polygonal and well annealed in small-scale fold hinges, and can be inferred to have undergone significant deformation with concurrent textural re-equilibration without change of phase composition or modal mineralogy. There are no relics in these rocks of any earlier fabrics. Besides the minor components of sphene, mica, rutile and opaques there is no evidence in most specimens of any extra phases having coexisted with glaucophane and epidote prior to the growth of the 'eclogite' minerals described below.

Garnet forms up to 15 per cent of the rock, almost invariably as large euhedral porphyroblasts grown over the glaucophane–epidote fabric (Fig. 3*a*). The garnets include

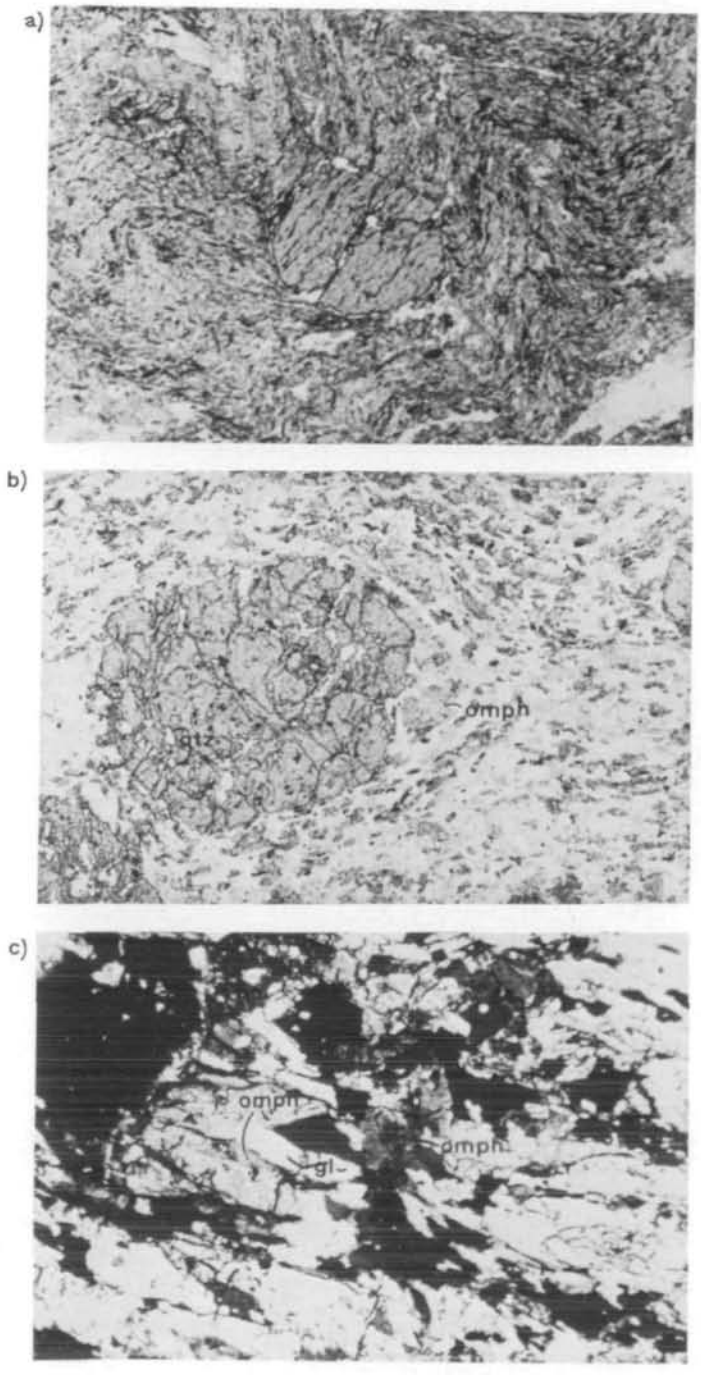

FIG. 3. (*a*) Typical garnet porphyroblast in the fine-grained gneissic metabasites. The garnet encloses straight inclusion trails of sphene (dark) and some epidote, and truncates the matrix glaucophane fabric. The tight folding in the matrix clearly postdates garnet growth (ppl, field of view—5 mm). (*b*) Garnet porphyroblast in a similar fine-grained glaucophane—epidote metabasite, here enclosing one, or perhaps two concentric zones of globular quartz inclusions. Quartz is absent in the matrix. The matrix fabric is in this case partially bowed around the porphyroblast. Note the late omphacite microporphyroblasts, also overprinting the glaucophane fabric (ppl, field of view—4 mm). (*c*) Omphacite growth over a polygonal glaucophane fabric. The omphacites are internally undeformed yet entirely enclose a relict of the tectonite glaucophane fabric (Xpl, field of view—2 mm).

sphene and epidote, both with a grain size similar to that in the matrix. In some samples the garnets also enclose globular grains of quartz (Fig. 3*b*), often concentrated in the porphyroblast core. Quartz in these rocks is only very rarely seen in the matrix.

The inclusion patterns vary between different samples. In many there are clear, straight inclusion trails, though these are often rotated with respect to the matrix schistosity (e.g. Fig. 3*a*). In only a few samples are there good sigmoidal trails. In some samples one can infer a two- or multi-phased garnet growth by the presence of concentric zones rich in quartz inclusions, or by an inclusion-rich core and an inclusion-poor overgrowth (Fig. 3*b*).

Omphacite is not seen in all samples. Where present it is generally slightly more abundant than garnet. It also clearly overprints the glaucophane–epidote fabric, characteristically as anhedral grains a few times the size of the matrix glaucophane and aligned subparallel to the foliation (Fig. 3*b*). In some samples a mesh of omphacite laths may entirely enclose relics of the polygonal glaucophane fabric (Fig. 3*c*).

In many samples omphacite shows clear intracrystalline deformation features. In some, however, the matrix schistosity has been re-formed and bowed around the garnet porphyroblasts yet the omphacite grains are sensibly internally undeformed. Omphacite is only seen as an inclusion phase in garnet in a small number of samples. These features both suggest that in such samples there has been significant garnet growth before the nucleation of omphacite. It is a general rule that where omphacite is deformed, or seen as inclusions in garnet, the garnets either show sigmoidal inclusion trails or have textures indicating two-phase growth.

Paragonite and phengite are seen in two textural sites: as small aligned grains spatially associated with epidote in the matrix, and as larger, late- or post-tectonic grains spatially associated with omphacite. In some samples there are late-tectonic omphacite–mica veins, and in many of these samples omphacite and mica are seen only in such veins.

PETROLOGICAL ANALYSIS

Form of the reaction: chemography and thermodynamics

The textures in the gneissic metabasites suggest a reaction forming garnet, omphacite, paragonite and quartz at the expense of glaucophane and epidote (cf. Reinsch, 1979). Using the phase compositions seen (Table 2), with coefficients consistent with the observed volumetric ratios of the product phases, the reaction can be written:

$$\begin{aligned} 1{\cdot}02\ &Ca_2Al_3Si_3O_{12}(OH) + 1{\cdot}0\ Na_2Ca_{0{\cdot}1}(MgFe)_{3{\cdot}1}Al_{1{\cdot}9}(Si_{7{\cdot}9}Al_{0{\cdot}1}O_{22})(OH)_2 \\ &= 0{\cdot}97\ Ca_{0{\cdot}825}(MgFe)_{2{\cdot}175}Al_2Si_3O_{12} + 1{\cdot}33\ Ca(MgFe)NaAlSi_4O_{12} \\ &+ 0.67\ NaAl_3Si_3O_{10}(OH)_2 + 1{\cdot}05\ SiO_2 + 0{\cdot}84\ H_2O \end{aligned} \quad (1)$$

This reaction can be visualised in Fig. 4: the gar–omph–par plane in NACF space is pierced by the gl–ep join.

The available thermodynamic data suggest that the 'eclogite' assemblage is stable at higher temperatures. Assuming that the entropy of mixing in the product assemblage is approximately the same as that in the reactants, the data (Table 3) give, for 15 kb and 500 °C:

$$\Delta S_{(1)} = 100\ J\ K^{-1}\ mol^{-1}$$

$$\Delta V_{(1)} = -1\ J\ bar^{-1}\ mol^{-1}$$

where gar–omph–par is the high entropy assemblage.

No attempt has been made to estimate rigorously the uncertainties on these values. All that is important in the context of this paper is the orientation of the reaction line in P–T space,

TABLE 2

Mineral analyses from a gl–ep–gar–omph–par–phengite metabasite

	Weight per cent oxides													
	Garnets					*Pyroxenes*				*Amphiboles*		*Epidote*	*Micas*	
	GT11A e	*GT11B* e/c	*GT11D* c	*GT12A* c	*GT12C* e	*PX11A* e	*PX11B* c	*PX14A* c	*PX14B* e	*AM13A* e	*AM14A* c	*EP12A*	*MU11A*	*MU31A*
SiO_2	37·85	37·53	37·50	36·86	37·82	55·65	55·02	55·48	55·26	58·26	57·60	37·93	49·91	47·63
TiO_2	0·04	0·18	0·19	0·16	0·09	0·05	0·07	0·07	0·06	0·03	0·04	0·12	0·28	0·05
Al_2O_3	21·45	21·24	20·96	20·75	20·98	10·40	9·24	11·27	10·18	11·61	11·45	27·03	27·98	40·12
Cr_2O_3				0·02	0·06	0·01	0·01	0·02	0·01	0·05	0·03	0·00		
FeO	*26·55	26·52	24·15	26·53	26·37	4·41	5·81	5·97	5·41	7·04	7·07	7·23	2·04	0·70
MnO	0·61	2·08	4·53	2·13	0·53	0·06	0·01	0·20	0·02	0·00	0·02	0·08	0·01	
MgO	4·63	2·84	2·22	2·55	4·28	8·39	9·24	6·60	8·05	11·88	11·94	0·07	3·44	0·14
CaO	8·08	9·36	10·09	9·70	8·70	12·89	13·54	11·09	12·72	0·58	0·77	23·39		0·13
Na_2O	0·04	0·04	0·06	0·04	0·05	7·12	6·66	8·14	7·08	7·35	7·15	0·02	0·91	6·95
K_2O						0·01		0·01	0·04	0·01	0·00	0·02	10·03	0·29
Total	99·26	99·79	99·69	98·74	98·88	98·98	98·95	98·83	98·83	96·80	96·07	95·88	94·59	95·64
	Cations per formula unit													
	24 (O)					*6 (O)*				*23 (O)*		*25 (O)*	*22 (O)*	
Si	5·971	5·954	5·969	5·928	5·995	1·992	1·984	1·991	1·989	7·924	7·897	5·995	6·667	5·978
Ti	0·005	0·021	0·023	0·020	0·011	0·001	0·002	0·002	0·002	0·003	0·004	0·014	0·029	0·005
Al	3·991	3·973	3·932	3·932	3·922	0·439	0·393	0·477	0·433	1·861	1·847	5·037	4·405	5·971
Cr				0·002	0·008					0·005	0·002			
Fe^{3+}	0·033	0·052	0·076	0·118	0·070	0·065	0·089	0·099	0·074	0·175	0·221	0·938	0·228	0·074
Fe^{2+}	3·471	3·466	3·139	3·450	3·425	0·069	0·087	0·080	0·088	0·626	0·589	0·018		
Mn	0·083	0·280	0·611	0·390	0·071	0·002	0·001	0·006		0·000	0·002	0·011	0·001	
Mg	1·089	0·671	0·526	0·612	1·011	0·448	0·462	0·353	0·433	2·407	2·438	0·017	0·683	0·027
Ca	1·367	1·591	1·722	1·671	1·478	0·495	0·524	0·427	0·492	0·085	0·113	3·961		0·018
Na	0·011	0·011	0·018	0·012	0·014	0·495	0·466	0·567	0·495	1·937	1·900	0·007	0·238	1·794
K										0·000	0·000	0·004	1·709	0·047
Total	16·020	16·019	16·016	16·035	16·005	4·005	4·008	4·002	4·009	15·023	15·014	16·000	13·961	13·914

The letters after the sample numbers above each column indicate separate analyses from a single grain. The letters 'e' and 'c' indicate whether the analyses are from the edge or core of a grain respectively. The recalculations to cations per formula unit follow the methods of Papike *et al.* (1974) for pyroxene, Holland & Richardson (1979) for amphibole, and otherwise site occupancy methods as described in Ridley (1982)—for garnets filling sequentially tetrahedral and octahedral sites up to 6·0 and 4·0 per unit, for epidotes the sum of cations up to 16·0, for mica tetrahedral and octahedral sites up to 12·0. The analyses are all wavelength dispersive analyses performed on the 'Cambridge Scientific Instruments Microscan 5' microprobe at Edinburgh University. Each element is standardised against a proven standard of simple composition. Corrections for atomic number, ZAF etc. follow Sweatman & Long (1969). A correction for

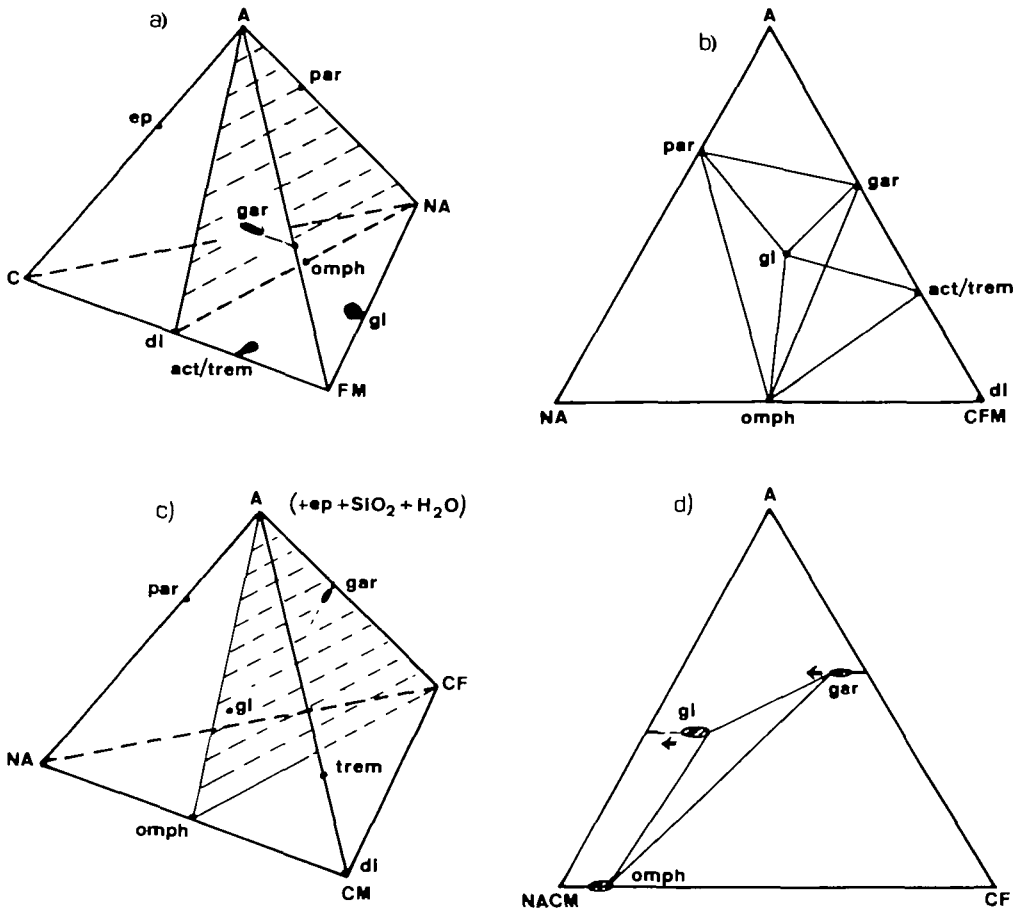

FIG. 4. Illustration of the form of the glaucophane—epidote to eclogite reaction (1). (*a*) Position of the phases in 'NACF' space. Components: A—Al + Fe^{3+}, C—Ca, FM—Fe^{2+} + Mg, NA—Na + Al + Fe^{3+}. (*b*) Projection from epidote onto the plane NA–A–CFM, the shaded plane of Fig. 4*a*. Note that glaucophane appears equivalent to omph + par + gar. (*c*) Expansion of the plane of Fig. 4*b* into a tetrahedron to separate iron and magnesium. Garnet is iron-rich, omphacite and glaucophane are both magnesium-rich. (*d*) Projection from paragonite onto the shaded plane of Fig. 4*c*, the plane A–CF–NACM, showing the three phase field of gar–omph–gl stability. The arrows show the direction of compositional shift with increasing temperature. The three phase field will move to more Mg-rich compositions with increasing temperature.

which for the reaction above is effectively isothermal. The actual values would be influenced by solid solution mixing and ordering in the various phases.

The chemography and entropy change of reaction (1) predict that for any constant a_{SiO_2} and a_{H_2O} there should be a temperature beneath which garnet and omphacite should not be stable in the presence of Na-mica, and above which glaucophane should not coexist with epidote.

Continuous nature of the reaction

The textures suggest that the reaction proceeded to varying degrees of completion in different samples. Reinsch (1979) in his study of similar metabasites from the Sesia-Lanzo zone of the Alps specifically reports an absence of the five phase assemblage gl–

TABLE 3

Volume and entropy thermodynamic data

	$V\ (cm^3)$	$S(J\ K^{-1}\ mol^{-1})$
Jadite	60·4	133·4
Diopside	66·09	143·0
Grossular	125·3	254·6
Pyrope	113·3	222·0
Glaucophane	262·2	538·5
Clinozoisite	136·2	296·0
Paragonite	132·53	278·0
Quartz	22·688	41·4
H_2O (15 kb and 500 °C)	16·08	123·2

Data are from Helgeson *et al.* (1978), with the addition of consistent revised glaucophane data from Koons (1982*a*) and 15 kb water data from Delany & Helgeson (1978).

ep–gar–omph–par, i.e. what would be a reaction assemblage in the four component system. This is, however, clearly present on Syros (Dixon, 1969), and has also been recorded from the neighbouring island of Sifnos (Schliestedt, 1980). Schliestedt shows that if ferrous iron and magnesium are treated as separate components then this five phase assemblage is an equilibrium assemblage. A 'reaction loop' (Fig. 5, after Ramberg, 1944; and Thompson, 1976) can be drawn for T–$X_{Mg/(Mg+Fe)}$ space, with a continuous reaction relating the 'glaucophanite' and 'eclogite' assemblages, and the five phase assemblage stable over a range of pressure and temperature for any specific Fe:Mg ratio. Reported Fe:Mg distribution coefficients for the phases at the temperature of interest (e.g. Schliestedt, 1980), and the observed ratios (Table 2) suggest that the garnet-bearing assemblage would be favoured by low Mg:Fe.

It is seen from the analyses of Table 2 that ferric iron and aluminium should likewise be treated as independent components. Fractionation of these ions between the two assemblages is such as to suggest that the glaucophane–epidote assemblage would be favoured by high Fe^{3+}:Al ratios. Unless there is a buffering of the ferric iron activity (for instance from an opaque phase), the system is trivariant, and at any specific temperature and pressure the Fe:Mg ratio of the various phases of the five phase assemblage will depend on the Fe^{3+}:Al ratio of the rock (Dixon, 1969).

Whether or not Fe^{3+} should be treated as an independent component the form of the reaction relationship illustrated in Fig. 5 remains unchanged. There will be a temperature interval over which the reaction is continuous. This exact interval, and the exact partitioning between the various phases will, however, be dependent on the Fe^{3+}:Al ratio of the rock.

The continuous nature of reaction (1) can be illustrated by projections in the NACFM system. A projection from epidote onto the plane NA–A–CFM (Fig. 4*b*) shows that glaucophane can be represented by paragonite, garnet and omphacite if Fe and Mg are thermodynamically indistinguishable. Garnet however is iron-rich; omphacite, and less so glaucophane, are magnesium-rich (Fig. 4*d*). The partition coefficients reduce with increasing temperature, the effective thermodynamic distinction between iron and magnesium is lessened and the range of possible par–gar–omph compatibilities will eventually encompass the range of glaucophane compositions. Similar principles apply if glaucophane rather than epidote remains stable throughout.

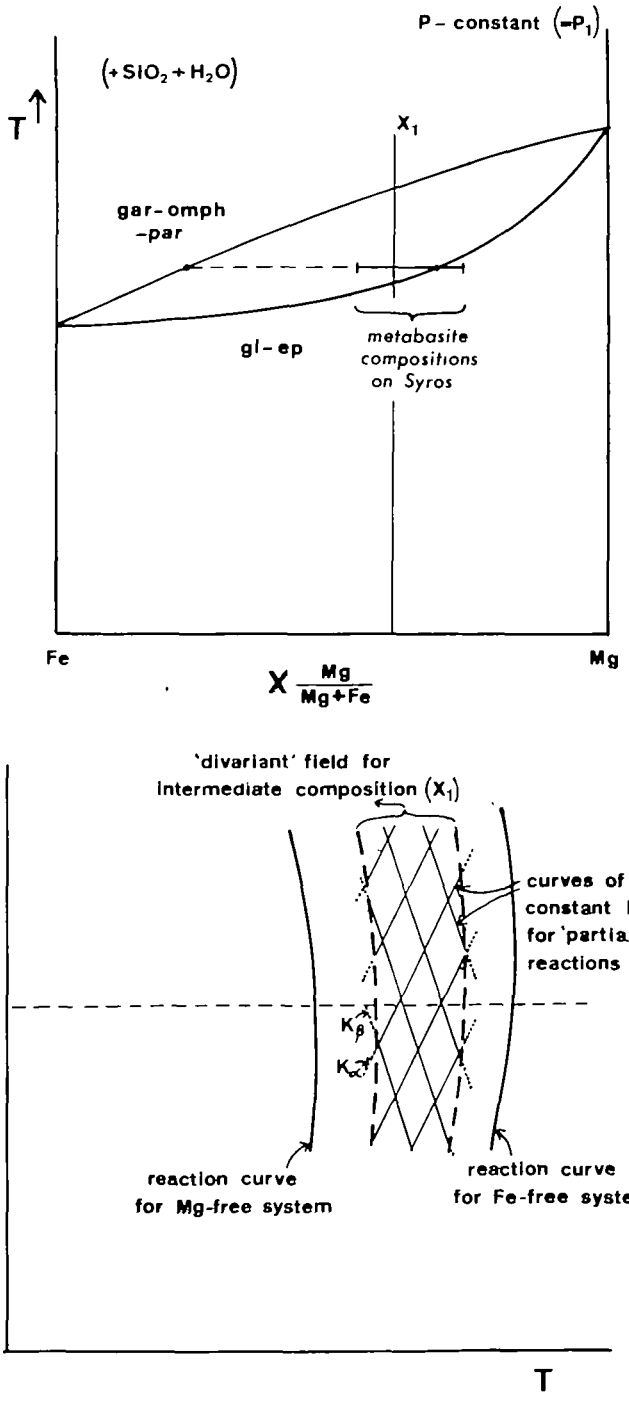

FIG. 5. Schematic T–$X_{Mg/Mg+Fe}$ section and P–T projection for the gl–ep–gar–omph–par system in NACFM with constant a_{SiO_2} and a_{H_2O}. Within the 'divariant' loop the compositions of the five phases may vary. These variations can be regarded as resulting from the changing equilibria of a series of net-transfer reactions with exchange components ('partial' reactions), schematically illustrated by the lines labelled Kα, Kβ etc. Any change in metamorphic conditions within the 'divariant' field will give a change in the proportions of reactants and products, and also through the changing equilibria of these 'partial' reactions, a change in the equilibrium compositions of all the phases.

EVIDENCE FOR DISEQUILIBRIUM DURING ASSEMBLAGE DEVELOPMENT

(*a*) *Timing of garnet and omphacite growth*

If complete equilibrium prevailed, the products of a continuous reaction such as reaction (1) should have grown simultaneously and progressively as the metamorphic conditions evolved. The textures suggest that in general this was not the case.

Inclusion textures in garnet imply that growth was not progressive. Garnets in all gneissic metabasites have grown over an already-developed planar tectonite glaucophane and epidote fabric, yet were often rotated after growth ceased. The structural style on Syros suggests a single progressive deformation event (Ridley, 1982), with incremental strain essentially shear parallel to the planar fabric. The garnets must therefore have grown within the time span of the deformation, and those with straight inclusion trails must have grown sufficiently fast for rotation during growth to be negligible (cf. Olesen, 1978). They cannot have grown before the deformation as the tectonite glaucophane–epidote fabric they overprint is itself a product of this deformation event.

The equilibrium proportion of products to reactants in a continuous reaction increases smoothly and continuously as the reaction loop (Fig. 5) is crossed. One possible cause of a more spasmodic growth, as inferred here, might be the delay in nucleation of a product phase, presumably because of a kinetic barrier to nucleation (McLean, 1965; Rubie, 1983). If nucleation is delayed there is the potential for initially rapid growth up to the then prevailing equilibrium proportions.

The textures also suggest that in many samples garnet nucleated before omphacite and paragonite. If the rock before the onset of reaction was bimineralic gl–ep, then if equilibrium was maintained garnet, omphacite and paragonite should all grow simultaneously.

There are a number of possible situations in which garnet would grow earlier even with equilibrium maintained. If the rock was not originally bimineralic gl–ep garnet would coexist below the temperatures of gar + omph + par stability in rock compositions in the volume gar–ep–gl–par; its most likely precursor in such compositions being chlorite. It is possible that some of the early garnet growth resulted from chlorite breakdown. Reaction (1) is, however, well balanced for the phase compositions and modal proportions of products seen in many samples. If a large proportion of the garnet grew after chlorite, the omphacite and paragonite must have grown from a now 'reacted out' sodium-rich phase. As no mineral of a suitable composition is known from blueschist terrains this is regarded as unlikely.

Alternatively balanced reactions of the form gl + ep $\rightarrow$ gar with exchange components, presumably in the glaucophane molecule, might have operated, e.g.

$$20\,\mathrm{gl} + 24\,\mathrm{ep} = 36\,\mathrm{gar}(\mathrm{Ca}_{1\cdot33}\mathrm{Mg}_{1\,67}) + 164\,\mathrm{qtz} + 40\,\mathrm{NaAlSi}_{-1} + 32\,\mathrm{H_2O} \qquad (2)$$

or

$$43\,\mathrm{gl} + 18\,\mathrm{ep} = 48\,\mathrm{gar}(\mathrm{Ca}_{0\cdot75}\mathrm{Mg}_{2\cdot25}) + 319\,\mathrm{qtz} + 21\,\mathrm{MgSiAl}_{-2} + 86\,\mathrm{NaAlSi}_{-1} + 52\,\mathrm{H_2O} \qquad (3)$$

or linear combinations of the two. It is seen, however, that the exchange components required always dominate the stoichiometry of the balanced reaction and would give an amphibole composition shift towards katophorite or eckermannite. Such a shift has never been recorded in blueschist amphiboles of this association.

Possible reasons for the apparently delayed growth of omphacite and paragonite involving disequilibrium processes are that:

(a) a metastable phase, e.g. richteritic amphibole, formed simultaneously with garnet, and

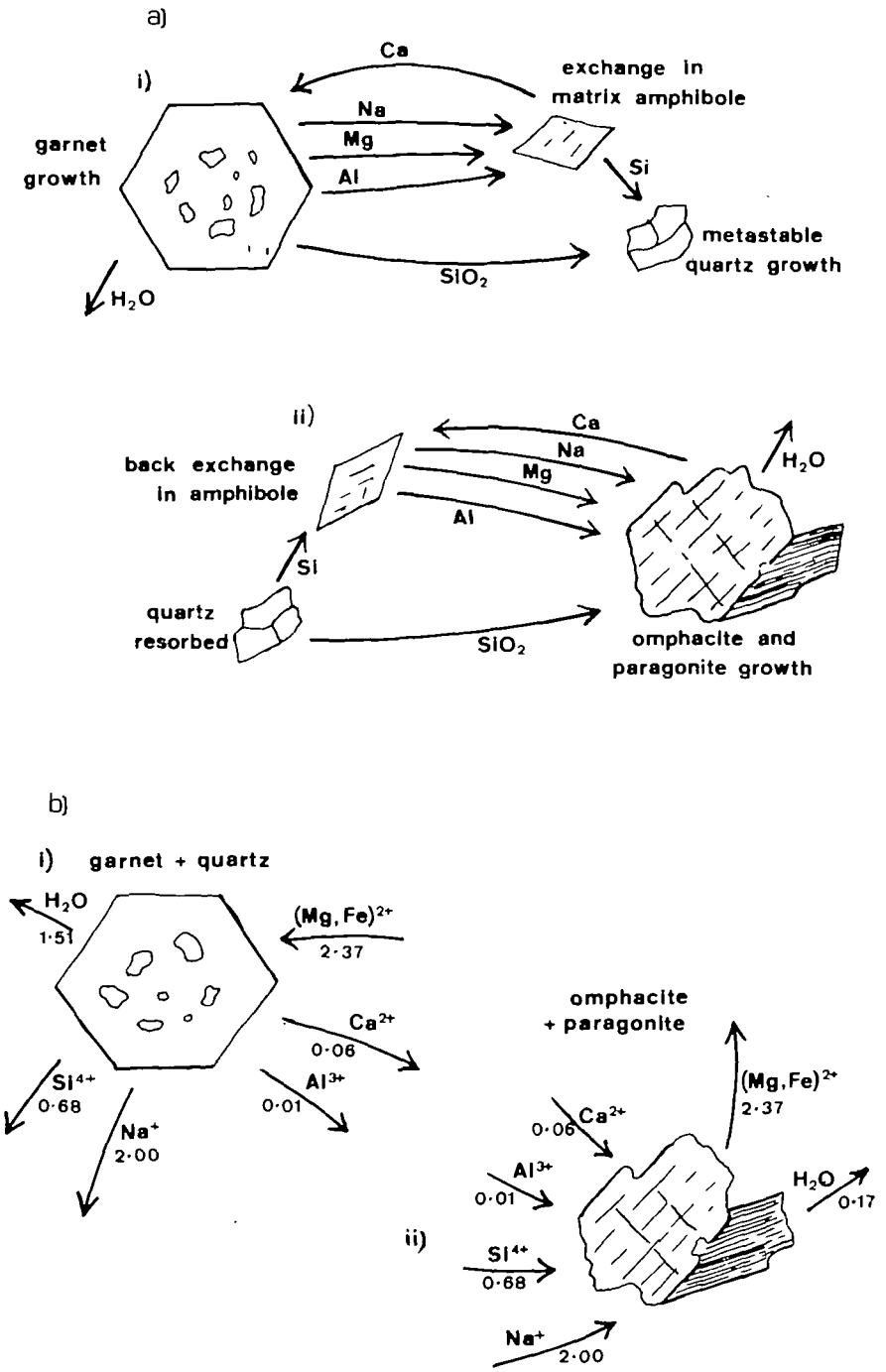

FIG. 6. Reaction mechanisms allowing a staggering of reaction (1). (*a*) Growth of intermediate metastable phases. It has been assumed in this case that the ratio of glaucophane and epidote reacting is such as to give quartz and a theoretically possible, but very unlikely amphibole in the matrix. The absolute exchange capacity (Thompson *et al.*, 1982) of amphibole is reached after about 5 per cent by volume reaction. (*b*) Exchange with a dispersed, or fluid phase (cf. Carmichael, 1969). The figures given are the moles of each cation exchanged per stoichiometric formula of the reactants. It is in such a history possible that the ratio of reactants would differ in the two halves of the reaction, or that the chemistry of the fluid phase would evolve as a result of the reaction.

subsequently reacted to give omphacite and paragonite so that no relic or textural trace of it is seen now in the rock (Fig. 6*a*);

(b) the omphacite + paragonite component was stored, latent, and therefore presumably in a fluid phase until crystallization (Fig. 6b);

(c) the problem is in part one of the scale of sampling—material was transported over distances greater than the scale of a thin section, and it is merely fortuitous that the samples studied have shown an early growth of garnet.

Whatever the history, however, it is clear that the omphacite and paragonite components released during garnet growth over glaucophane and epidote did not nucleate as these phases where and when first released. These components were either transported over distances greater than the scale of a thin section, or were held metastably in solution or in solid phases. Because is some samples omphacite–paragonite veins are seen, and because these two phases are in general seen together on a thin-section scale, either the second or third possibility above is regarded as the most likely. If the relevant components are held in solution, then even if the solutions are hypersaline (fluid inclusion work on Syros suggests this, R. D. Schuiling, pers. comm, 1983) a significant percentage by volume of rock is implied.

(*b*) *Disequilibrium implied by mineral zonation patterns*

Reaction (1) was written assuming that the compositions of all the phases participating were fixed. It is possible to write a set of independent reactions each involving one or more fewer phases than reaction (1) and balanced by exchange components acting in one or more phases ('net-transfer' reactions of Thompson & Thompson, 1976, and Thompson *et al.*, 1982). If equilibrium is maintained, then under changing metamorphic conditions there should be systematic changes in the equilibria of each of this set of reactions. These variations will be reflected by the mineral zonation patterns. These reactions have the extra property that, because they involve less than the full number of reacting phases in the rock, changes in mode are not directly related to the shifts in reaction equilibria. Because of this property they are termed here 'partial' reactions. The number of independent reactions is a function of the sum of the number of independently variable components in each phase (Thompson *et al.*, 1982).

An alternative way of looking at this is that the stoichiometry of reaction (1) is specific to a unique set of conditions (*P*, *T*, etc). If these conditions are altered then not only will 'reaction' take place, but there will also be changes in the compositions of reactant and product phases, and hence also of the stoichiometry of the reaction (Fig. 5).

The phases most markedly zoned in the rocks considered are garnet and omphacite. In the reduced, NACF, system each phase has two end-member components: gro + pyr in garnet, and di + jd in pyroxene. In the five phase, four component system there are therefore two independent net-transfer, partial reactions. All the samples discussed below show the five phase assemblage gl–ep–gar–omph–par.

One net-transfer reaction illustrating the control on the Ca content of the garnet is:

$$2\ \text{pyr} + 5\ \text{CaMg}_{-1} + \text{qtz} + \text{par} = 2\ \text{clz} + \text{omph} \qquad (4)$$

Reaction (1) was written assuming a constant garnet composition. A series of very similar reactions can be written each producing a garnet of slightly different composition and with slightly different ratios of the other participating phases, i.e. reaction (1) plus or minus proportions of reaction (4).

Assuming all phases except for garnet have pure end-member compositions then the equilibrium constant for the above reaction can be written as:

$$K_{(4)} = (a_{\text{MgCa}_{-1}})^5 (a_{\text{pyr}})^{-2}$$

The available thermodynamic data suggest that the garnet formed should become less grossular-rich with increasing temperature:

$$\Delta S_{(4)} = 35 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta V_{(4)} = -0{\cdot}3 \text{ J bar}^{-1} \text{ mol}^{-1}$$

This result will be independent of the specific reaction chosen amongst the five relevant phases. If the bulk rock reaction (1) was promoted by increasing temperature, the garnets should show zonation towards less grossular-rich rims. Although reaction (4) itself suggests that garnet should decrease in mode with increasing temperature, this reaction is taking place concurrently with reaction (1) producing garnet and omphacite from glaucophane and epidote. The net effect is of increasing modal garnet.

Those samples that show evidence for simultaneous garnet and omphacite growth, and for a phased garnet growth do show a calcium depletion towards the garnet rims, by about 3–4 per cent mol end-member (Fig. 7). (The textures of garnet suggest that it was a product phase of the reaction taking place. The zoning patterns cannot therefore be the result of diffusion between garnet and an evolving matrix; Anderson & Buckley, 1973; Loomis, 1975).

Manganese in such garnets, as is usual at these metamorphic temperatures, is concentrated in the grain cores. There seems no reason to depart from the normal interpretation that this is the result of fractionation of available manganese into garnet on growth (Harte & Henley, 1966; Hollister, 1966).

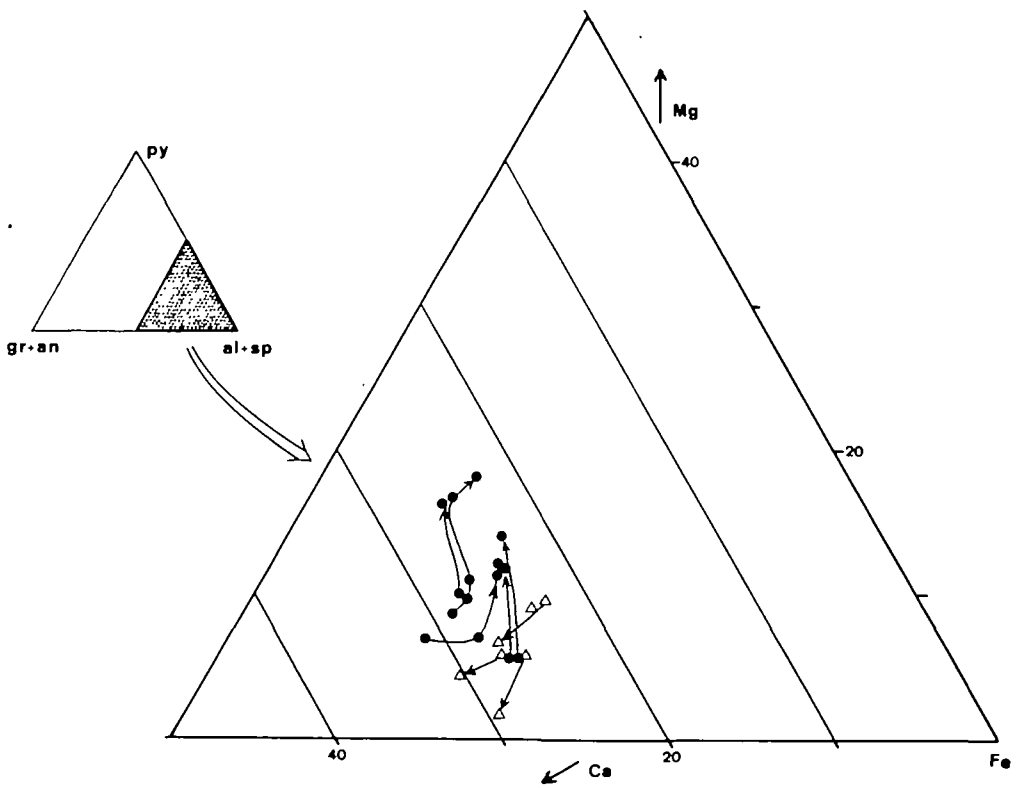

FIG. 7. Garnet zonation patterns in gl–ep–gar–omph–par metabasites from Syros. The normal pattern (filled circles) is for increasing Mg, and decreasing Ca towards the rims. Some samples however show a reversed pattern (open triangles) with increasing Ca and decreasing Mg towards the rims.

The zonation patterns in garnets for which the textures suggest a single period of rapid growth, and for which there are no indications of simultaneous omphacite growth, contrast with those described above (Fig. 7). In these there is an Mg depletion, and an Mn and Ca enrichment in the rims. This is the pattern demonstrated by de Bethune *et al.* (1975) to be formed during retrogressive replacement of garnet involving chlorite. Such an overprinting is seen locally on Syros, but not by any means in all the samples showing this reverse zoning.

If, as is suggested, both sets of garnets grew as a result of the same reaction (i.e. with equilibrium between the same five phases everywhere close to the same composition), then it is clear that both zonation patterns cannot simultaneously be recording a history of changing P–T conditions. A rapidly grown grain should not record any history of changing equilibrium conditions during growth. Any zonation in such a grain must be the result of a disequilibrium process. This is as implied here. The grains showing textures suggesting rapid growth show zonation patterns inconsistent with the up-temperature evolution inferred from the general direction of reaction. The grains showing evidence of phased growth show zonation patterns consistent with up-temperature evolution.

There is an independent 'partial' reaction that illustrates the control of the diopside:jadeite ratio of the pyroxene, assumed above to be stoichiometric omphacite (cf. Table 2). This can be written as;

$$\text{omph} + 4\ \text{par} = 2\ \text{gro} + 2\ \text{pyr} + 5\ \text{NaAlCa}_{-1}\text{Mg}_{-1} + 4\ \text{qtz} + 4\ \text{H}_2\text{O} \qquad (5)$$

for which:

$$\Delta S_{(5)} = 240\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta V_{(5)} = -6\ \text{J bar}^{-1}\ \text{mol}^{-1}$$

(with jadeite and garnet on the high entropy, low volume side), i.e. the pyroxene phase should become more jadeitic with increasing temperature.

Even where the garnet zoning is consistent with up-temperature metamorphism there is not the clear trend that this reaction suggests ought to be present (Fig. 8). In one sample analysed the pyroxene rims show a sensibly invariant composition close to stoichiometric omphacite, but the small magnitude zoning is in different grains from either more-jadeitic or less-jadeitic pyroxenes. There are no textures indicating whether omphacite growth was rapid or slow. This 'convergent' zoning may be the result of early growth equilibrating only with a very local environment whilst the rims grew equilibrated with, or have equilibrated with the bulk rock conditions. Data from a similar sample, but with a higher Fe^{3+}:Al ratio are also plotted on Fig. 8. In this there is a slight increase in jadeite content towards the pyroxene rims.

No zoning has been found in the matrix glaucophane and epidote. This could be the result of buffering, a high degree of ordering within amphibole (Koons, 1982*b*), or very slow or very fast intracrystalline diffusion rates. Because of this uncertainty the analysis above has concentrated on equilibria that do not involve exchange in the reactant phases.

POSSIBLE METASOMATIC EFFECTS OF THE SERPENTINITE BODIES

The same suite of minerals is seen in the blocks enclosed within serpentinite as in the rest of the meta-igneous suite. There are however a wide variety of reaction and replacement textures (Dixon, 1969). Textures implying both glaucophane growth over omphacite, and the converse are seen. Dixon has shown that the inferred reactions are qualitatively consistent with likely cation metasomatism driven by reactions and equilibria in the serpentinite bodies.

More pertinent for the discussion here are the observations on the assemblages of the interiors of the blocks. These are essentially either glaucophane–eclogites without epidote, or

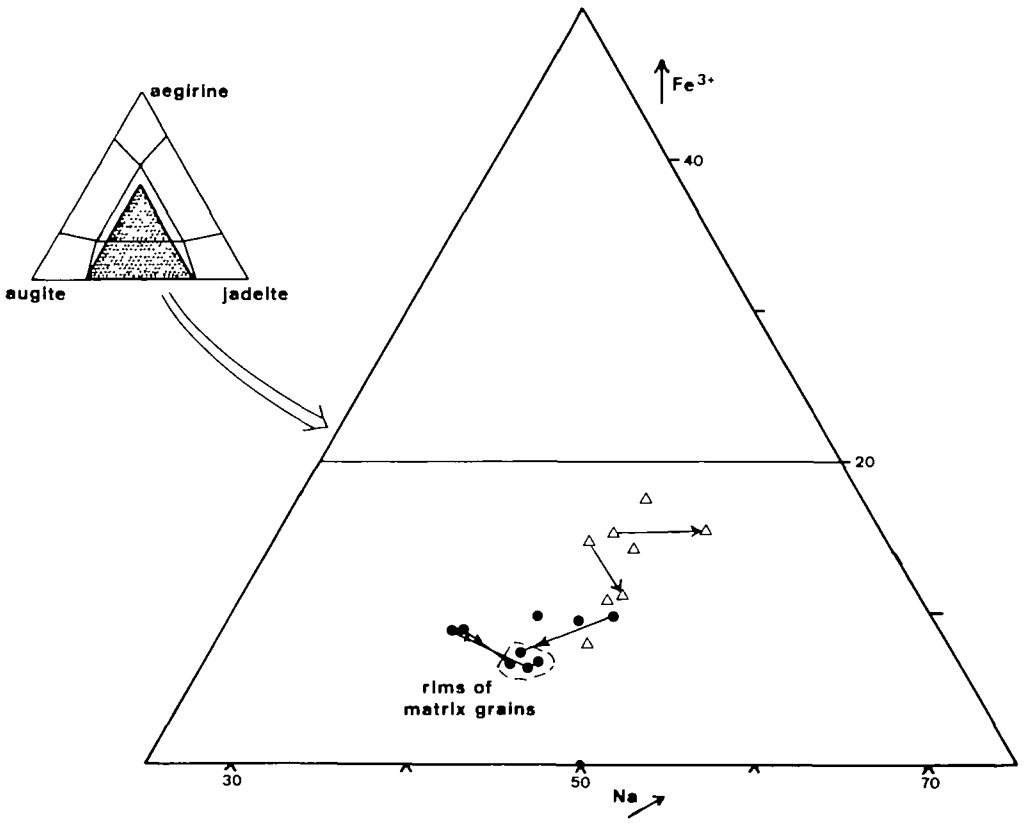

FIG. 8. Pyroxene compositions and zonation patterns in metabasites from Syros. The data come from two samples. The filled circles are from a sample in which growth of garnet and omphacite was apparently simultaneous—omphacite is here seen as inclusions in garnet. Zonation in this case is always towards a constant rim composition. The other sample (open triangles) shows similar textures but the rock has a higher Fe^{3+}:Al ratio. In this there is a slight increase in the jadeite content of the pyroxenes towards their rims.

epidote–mica–eclogites without glaucophane, i.e. the assemblages predicted as the end products of reaction (1). It is only in the blocks enclosed within serpentinite that metabasites are seen without the coexistence of glaucophane and epidote.

The compositions of the phases are little different from those in the gl–ep bearing metabasites. The relative promotion of reaction (1) here seems most likely to be the result of reduced silica activity (Dixon, 1969).

Reactions seen to be taking place within serpentinite bodies involve the formation of talc, chlorite, and locally actinolite or a carbonate phase. The antigorite to talc reaction provides a silica activity buffer. The calculations of Hemley *et al.* (1977) suggest that at the conditions of interest (15 kb and 500 °C) at this buffer $a_{SiO_2} = 0{\cdot}1$. Such a silica activity would shift the position of equilibrium for reaction (1) by almost 200 °C in the direction of stabilizing gar–omph–par at lower temperatures.

In the meta-igneous suite on Syros no rock is more than 100 m away from the projected position of a serpentinite body. The activity of silica need only be reduced below unity, and not necessarily buffered over this distance in order to promote reaction (1) as seen in these rocks.

Is reaction (1) promoted by decreasing a_{SiO_2} or by increasing temperature? Free quartz is

found within the metabasites, but in general only within and immediately adjacent to the garnet porphyroblasts. This therefore is not conclusive evidence that quartz was stable. Quartz is liberated by reaction (1) or by the direct replacement of glaucophane by garnet. Its preservation in and around garnet could be related to sluggish diffusion rates. As the magnitude of such are totally unknown no estimate of a minimum silica activity for the matrix can be made.

More critical evidence that silica activity remained high is found in the garnet zonation patterns. The equilibrium of the reaction proposed controlling the grossular content of the garnet (reaction 4) provides a petrological marker in that the effects of reduced silica activity and prograde metamorphism are opposed. Garnet should become more grossular-rich if the reaction is promoted entirely by reduced silica activity and less grossular-rich if the reaction is promoted by up-temperature metamorphism.

SYNTHESIS AND DISCUSSION

The reaction observable in the rocks producing garnet and omphacite at the expense of glaucophane and epidote could have been promoted by increased temperature, decreased water activity (see Brown & Bradshaw, 1979), or changes in the activities of certain cations (notably a decrease in a_{SiO_2}). The reaction is continuous. It would under equilibrium conditions be progressive with a progressive change in any of the above listed variables.

Because of the large number of interacting exchange reactions in the participating phases the exact stoichiometry of reaction (1) will be uniquely determined by P,T, and the activities of all the participating species. It should theoretically be possible to determine which thermodynamic parameter changed so as to promote the observed reaction by studying the complete zonation patterns of the minerals present. The zonation should, under equilibrium conditions, reflect the changing stoichiometry of the gross reaction.

It is a corollary of the above, that if the change in the metamorphic conditions was progressive in all rocks with respect to the same variables (whichever of P, T, a_{H_2O}, a_{SiO_2}, etc), then so long as the reaction continued to involve the same phases the sense of the zoning should be constant over the whole rock suite, and should in each phase remain in the same direction. On Syros the whole rock suite must have undergone essentially identical P–T histories. There is a set of samples in which the bulk-rock reaction and the zonation patterns of garnet and omphacite are all consistent with up-temperature metamorphism. In these samples the textures imply both some overlap of growth of all the bulk-rock reaction products, and a relatively projected period of product growth. Because these are the textures most consistent with an equilibrium response to any gradual change in the imposed metamorphic conditions, they are regarded as indicating that the rocks did undergo an interval of up-temperature metamorphism.

Unless the up-temperature part of the reaction loop of Fig. 5 is metastable with respect to alternative assemblages (e.g. barroisite-bearing assemblages) the implication is that eclogitic assemblages can be formed from 'blueschists' during prograde high-pressure metamorphism. The distinction between 'eclogites' and 'blueschists' in a regional metamorphic terrain can be indicating different P–T conditions of metamorphism.

There are however also samples which, despite showing the same bulk-rock reaction, show garnet and omphacite zonation patterns inconsistent with simply up-temperature metamorphism. These complexities may reflect the local influence of variables such as a_{SiO_2} during the evolution of the rocks. Certainly a_{SiO_2} does seem to have had an affect on the evolution of the blocks enclosed within serpentinite. The preceeding discussion, however, suggests that it is unlikely to have had an effect on the gneisses in general, and it is thought that the zoning complexities are largely the result of chemical disequilibrium during rock development. The

aspects of the mineral textures that suggest non-equilibrium behaviour, (the rapid growth of grains, and the asynchronous growth of the product phases), together with the complexities of the zonation patterns are all consistent with the major 'barrier' to equilibrium behaviour being that of phase nucleation (cf. Lacy, 1965; Spry, 1969).

The form of the reaction predicts steady product growth. The textures are more consistent with at least initially rapid growth of garnet and omphacite once these phases nucleated. It is obvious that a rapidly grown mineral will not preserve a record of a long metamorphic history. If there was a steady evolution of metamorphic conditions then a rapidly grown mineral would not register zoning associated with this evolution. Any zoning seen must reflect non-equilibrium effects such as the availability of cations, and cation diffusion rates.

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